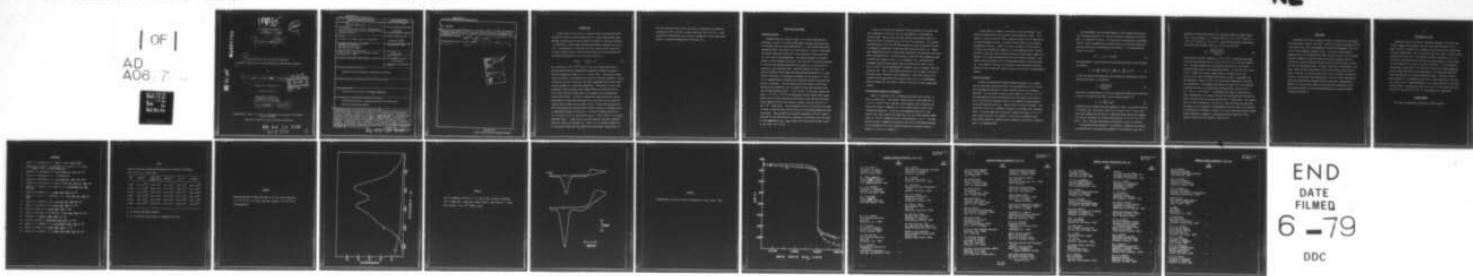
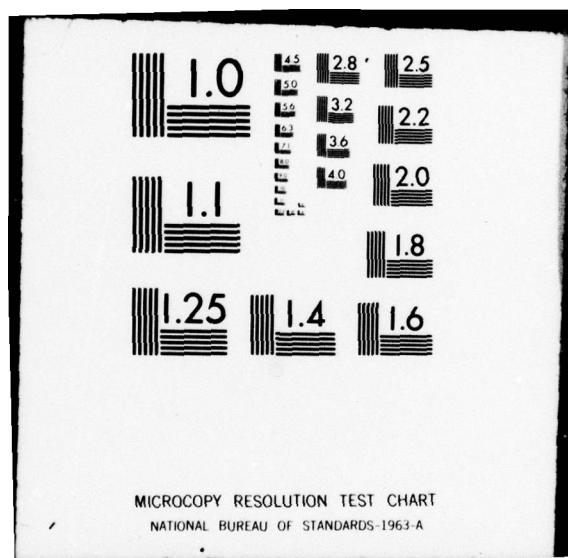


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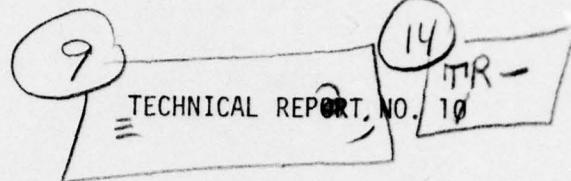
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6 ELECTROCHEMICAL AND SPECTRAL INVESTIGATIONS  
OF Ni(II) ION EQUILIBRIA IN ROOM TEMPERATURE CHLOROALUMINATE SOLVENTS.

by

10 R. J. GALE, B. GILBERT AND R. A. OSTERYOUNG

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## 20. ABSTRACT

consistent with  $\text{NiCl}_4^{2-}$  formation in the basic region. At  $40^\circ\text{C}$ , the  $\text{Ni}/\text{Ni(II)}$  standard electrode potential on the mole fraction scale was determined to be  $+0.800 \pm 0.005$  V (vs. 2:1 Al reference), and an equilibrium constant for the dissociation reaction,



was determined to be  $1.2 \pm 1.0 \times 10^{-46}$  up to the  $-46$ th power.  
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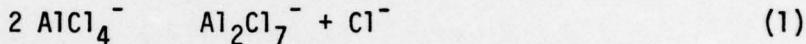
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INTRODUCTION

Certain molten salt mixtures of aluminum chloride and alkylpyridinium halides are liquid at ambient temperatures in a broad compositional range, thereby providing unusual ionic solvents for studies of acid-base chemistry, ion complexation, electrochemically generated organic compounds, etc. [e.g., 1-4]. A potentiometric investigation of the aluminum species equilibria in  $\text{AlCl}_3$ :1-butylpyridinium chloride (1-BPC) melts [1] has established that the equilibrium constant for the solvolysis reaction,



has a value of  $K_3 \leq 3.8 \times 10^{-13}$  at 30°C, the limit arising because the 1-butylpyridinium cation is spontaneously reduced by elemental aluminum in the basic composition range (i.e., <1:1  $\text{AlCl}_3$ :1-BPC). The extent of formation of the  $\text{Al}_2\text{Cl}_7^-$  ionic species was found to be decidedly enhanced in  $\text{AlCl}_3$ :1-BPC melts over that existing in the higher temperature  $\text{AlCl}_3$ :alkali metal chloride systems for a particular temperature. Additionally, the main disadvantage of the high  $\text{Al}_2\text{Cl}_6$  vapor pressure found with the acidic  $\text{AlCl}_3$ :alkali metal chloride systems seems to be negated in the corresponding organic halide melts. In order to substantiate these conclusions, further potentiometric studies have been made with a metal which is not capable of reducing the pyridinium cation, namely nickel. Gilbert and Osteryoung [5] have investigated the electrochemistry of Ni(II) species in the  $\text{NaAlCl}_4$  melt at temperatures between 175 and 210°C. The Ni(II) standard potential at 175° in a melt of  $\text{pCl}^- 5.8$  was found to be  $E_0 = 1.433 \pm 0.002$  V vs. Al reference (NaCl satd.). Fremont *et al.* [6] have reported a half-wave potential value for Ni(II) ion reduction,  $E_{1/2} = +0.83$  V vs. Al reference (60:26:14), in the eutectic fused salt  $\text{AlCl}_3:\text{NaCl}:\text{KCl}$  60:26:14 mole%, respectively, at

140° and find that Ni(II), Co(II) and Fe(II) ion reduction at the DME are irreversible, with a cathodic transfer coefficient for Ni(II) of  $\alpha = 0.88$ . The Ni-NiCl<sub>2</sub> electrode has been tried as a cathode for a solid electrolyte battery, at operating temperatures of 600-1000° [7].

RESULTS AND DISCUSSIONAbsorption Spectra

Anhydrous  $\text{NiCl}_2$  was soluble in basic ( $<1:1 \text{ AlCl}_3:\text{1-BPC}$ ) and with difficulty in acidic ( $>1:1 \text{ AlCl}_3:\text{1-BPC}$ ) melts, the basic solutions being sea-green/blue and the acidic sandy-colored. A light colored precipitate sometimes formed in the acidic melts upon standing. Figure 1a illustrates the optical absorption spectrum of a dilute solution of  $\text{NiCl}_2$  dissolved in a 0.8:1 melt at room temperature. The spectrum appears to be intermediate to those obtained from  $\text{NiCl}_4^{2-}$  ions dissolved in pyridinium chloride at  $160^\circ$  and that obtained from those ions present as a solid-solution in  $\text{Cs}_2\text{ZnCl}_4$  at room temperature [8]. Absorption spectra of nickel ionic species in molten chloride media have been studied extensively [8-11] and, based on these data, an unambiguous assignment for the spectrum in Figure 1a to a (approximately) tetrahedrally coordinated tetrachloronickelate ion species is possible. The most intense absorption doublet at 705 nm and 658 nm and the shoulder at  $\sim 617$  nm (Figure 1a) have been assigned to the spin-allowed absorption  $^3\text{T}_1(\text{F}) - ^3\text{T}_1(\text{P})$  [8-10]. For the  $\text{NiCl}_2$  composition range  $1 \times 10^{-3}$  to  $1 \times 10^{-2}$  M, the Bouger-Beer law was obeyed within experimental error and molar extinction coefficients for the 658 and 705 nm band maxima computed from the least-squares straight lines were 169 and  $175 \text{ L mol}^{-1} \text{ cm}^{-1}$ , respectively. These absorbance values are consistent with those of Smith, Liu and Griffiths [9] for  $\text{NiCl}_2$ /tri-1-butylbenzylphosphonium chloride systems. They reported that increasing temperature ( $22$ - $172^\circ$ ) caused a blue shift in the band maxima and a decrease in absorbance values such that at room temperatures  $A_{707} > A_{660}$ , whereas both maxima had the same A value of  $156 \text{ L mol}^{-1} \text{ cm}^{-1}$  at  $172^\circ$ .

Figure 1b illustrates the spectrum of  $\text{NiCl}_2$  dissolved in an acidic melt and a weak band at  $\sim 547$  nm was the only one detected in the 400-800 nm spectral range. Øye and Gruen [12] have studied the absorption spectra of dipositive nickel in molten  $\text{Al}_2\text{Cl}_6$  at  $227^\circ$  and 5.6 atmospheres. The spectrum exhibited bands at 476, 926, and 1563 nm which have been interpreted in terms of octahedral coordination of chlorides about the central metal ion. Temperature dependent equilibria involving both tetrahedral and octahedral states have been investigated [11] in  $\text{LiCl}-\text{KCl}$  mixtures at  $400-700^\circ$  and an absorption band at 448 nm was assigned to  $\text{Ni(II)}$  in an octahedral site. Absorption band assignments have also been made for  $\text{Ni(II)}$ -chloride anions ( $\text{NiCl}_2^+$ ,  $\text{NiCl}_2$ ,  $\text{NiCl}_3^-$ ,  $\text{NiCl}_4^{2-}$ ) and the  $[\text{Ni}(\text{DMSO})_6]^{2+}$  octahedral cation in dimethyl sulfoxide solutions [13]. None of these peaks correlates to the one found for  $\text{Ni(II)}$  in the acidic  $\text{AlCl}_3:1\text{-BPC}$  melt at room temperature. This result could be consistent with the supposition that divalent nickel ion is in an uncomplexed state or perhaps only very weakly solvated in the acidic solvent (vide infra studies).

#### Electrochemical Behavior of Nickel(II)

Figure 2 illustrates cyclic voltammograms obtained from solutions of  $\text{NiCl}_2$  in acidic melts. The cathodic current peak for nickel deposition at  $\sim +0.3$  V vs.  $\text{Al}(0)$  2:1 melt reference, shifts negative with increasing scan rate at  $40^\circ$ , which is diagnostic of a slow charge-transfer reaction rate (irreversible behavior). Unlike the high temperature case [5], on the reverse scan a small anodic wave comprising  $\sim 7\%$  of the total cathodic charge occurs at  $\sim +0.44$  V, preceding the bulk stripping peak at  $\sim +0.7$  V. The small peak may be due to codeposited aluminum in the nickel electrodeposit because of the proximity of the nickel species reduction to background aluminum reduction ( $\sim -0.15$  V on vitreous C).

In basic melts at vitreous C electrodes, no wave for  $[\text{NiCl}_4]^{2-}$  anion reduction appeared within the accessible solvent potential limits. This behavior is contrary to that found in organic solvents such as acetonitrile or dimethylformamide [14-15]. Florence [14] has reported a well-defined polarographic wave ( $E_{1/2} = -0.400$  V vs. SCE) in methanolic lithium chloride solutions with the  $[\text{NiCl}_4]^{2-}$  complex ion as the predominant Ni(II) species. Similarly, Ciana and Furlani [15] have studied the polarographic behavior of  $[\text{NiCl}_4]^{2-}$  ion in DMF and proposed that the nickel species reduction is preceded by rapid dissociation of the tetrahalogeno complex to the halid-free ion. The slowness of the rate of conversion to the electroactive form may explain the lack of  $[\text{NiCl}_4]^{2-}$  species reduction in the basic room temperature solvent.

#### Equilibria Studies

In order to determine the standard reduction potential,  $E_0$ , a Nernst plot was obtained by varying the nickel ion concentration in a 1.5:1 acidic melt and measuring the emf of a nickel electrode versus an Al reference electrode. For the nickel ion mole fraction range  $1.5 \times 10^{-5}$  to  $2.0 \times 10^{-3}$  the least squares slope was calculated to be 31 mV (theory value  $RT/2F$  at  $40^\circ$  is 31 mV) and the intercept value for the standard electrode potential on the mole fraction scale,  $E_0 = +0.800 \pm 0.005$  V versus Al reference. The activity of Ni(II) ion is assumed to be equal to the added Ni(II) concentrations. It may be noted that in the acidic composition range (1.5 to 1.1:1 molar ratio) the nickel ion potential is practically unaffected by the melt acidity (Figure 3), despite relative changes in the  $[\text{AlCl}_4]^-$ ,  $[\text{Al}_2\text{Cl}_7]^-$ , and  $\text{Cl}^-$  ion concentrations.

Emf measurements have been made between a nickel working electrode and an Al reference electrode as a function of the melt composition and typical data is illustrated in Figure 3. On the basis of the absorption spectroscopy results, it may be assumed that the major nickel ion equilibrium reaction in the basic melts can be represented by the formation of a single halonickel complex ion,  $\text{NiCl}_4^{2-}$ ,



The potentiometric curve may then be expressed approximately by the following relationship,

$$E = E_0 + \frac{RT}{2F} \ln [\text{NiCl}_4^{2-}] + \frac{RT}{2F} \ln K - \frac{RT}{2F} \ln [\text{Cl}^-]^4 \quad (3)$$

in which the species activities have been replaced by concentrations and the equilibrium constant K is defined by,

$$K = \frac{[\text{Ni}^{2+}][\text{Cl}^-]^4}{[\text{NiCl}_4^{2-}]} \quad (4)$$

The nickel ion concentrations in the basic composition range can be calculated at each of the measured emf values from the Nernst equation (5),

$$E = E_0 + \frac{RT}{2F} \ln a_{\text{Ni}^{2+}} \quad (5)$$

provided that the standard electrode potential is known. As the mole fraction of chloride ions is the excess 1-BPC--that in excess of the 1:1 molar ratio minus that combined with the Ni(II)--a mean equilibrium constant for equation (2) could be calculated for the basic datum points,  $\bar{K} = (1.2 \pm 1.0) \times 10^{-46}$  (40°). Table I contains representative calculations of the ion fractions.

From the equilibrium constant, it is possible to determine the chloride ion concentration at the equivalence midpoint of the potential break and to

determine the equilibrium constant,  $K_3$ , for the aluminum ion species equilibria. At the midpoint,  $E_e = +0.080$  V,  $[Ni^{2+}]_e = 6.71 \times 10^{-24}$ ,  $[NiCl_4^{2-}] = 1.70 \times 10^{-3}$ , and  $[Cl^-]_e = 4.18 \times 10^{-7}$ . Using the mass balance relationship at the equivalence point,  $[Al_2Cl_7^-]_e = [Cl^-]_e$ , and defining

$$K_3 = \frac{[Al_2Cl_7^-][Cl^-]}{[AlCl_4^-]^2} \quad (6)$$

the equilibrium constant becomes  $K_3 = 1.74 \times 10^{-13}$ , in reasonable agreement with the values reported earlier ( $K_3 \leq 9.5 \times 10^{-13}$  for 40° and ideal behavior [1]). The model assumes that the tetrachloronickelate ion is the major Ni(II)-chloride species in the equivalence region. For the basic emf values at 55°, a graph of emf versus  $\log[Cl^-]$  gave a straight line of slope  $0.135 \pm 0.011$  V and a correlation coefficient of 0.995, in agreement with the theoretical slope of 0.130 V for a fourth-power dependence on chloride ion concentration. The standard free energy of formation of the tetrachloronickelate anion may be calculated from the equilibrium constant, at 40°,  $\Delta G^\circ = -RT \ln K = 274$  kJ mol<sup>-1</sup>. Assuming that this model is appropriate at higher temperatures,  $\Delta G^\circ$  values at 120 and 150° were determined from potentiometric titration curves to be 291 and 304 kJ mol<sup>-1</sup>, respectively. The standard state for these calculations is Ni(II) ion in the acidic melt and there does not appear to be any comparative thermodynamics data for  $NiCl_4^{2-}$  ion formation in the molten salt literature. However, it is well known that transition metal halogen complexes of symmetry  $T_d$  do have appreciable stability in polar organic solvents with the absence of water [13,15].

CONCLUSIONS

Consistent with previous studies of Ni(II) in chloride-rich ionic media with large organic cations, the  $\text{NiCl}_4^{2-}$  complex ion forms as the major species in the basic  $\text{AlCl}_3$ :1-BPC room temperature solvent with apparently little distortion from tetrahedral symmetry of [8]. This may be rationalized by arguments similar to those advanced by Øye and Gruen [17] for  $\text{CoCl}_4^{2-}$  species formation, whereby the dipositive 3d ions are able to combine with free chloride ions and the large electrostatic repulsion energies favor the four-over the six-coordination state. A drastic difference is encountered in the acidic region and the solvent Al(III) ions, present almost exclusively as  $\text{Al}_2\text{Cl}_7^-$  and  $\text{AlCl}_4^-$  [1] can only exert weak, if any, influence on the Ni(II) ion core. The nature of such interactions is far less clear; nevertheless, the equilibrium constants obtained from the simple model represented by equation (2) lead to values which are consistent with estimations of the equilibrium constants for the chloroaluminate species using an aluminum indicator electrode [1].

EXPERIMENTAL SECTION

Anhydrous  $\text{NiCl}_2$  was obtained by sublimation separation from  $\text{NH}_4\text{Cl}$  [18] and the preparation of materials and melts have been described in earlier papers from this laboratory [1]. Because of the low volatility of these melts at working temperatures, even in the acidic composition range, a simple electrochemical cell may be used. The aluminum reference electrode was a coil of wire (Alfa, m5N) separated from the main cell compartment by a fine porosity frit and immersed in 2:1 molar ratio  $\text{AlCl}_3$ :1-BPC melt. For potentiometric measurements a nickel wire (Alfa, m3N7) was cleaned with a  $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4/\text{HNO}_3$  mixture, washed and dried at room temperature. All experiments were made under purified argon in a Vacuum Atmospheres drybox. Absorption spectra were recorded in 1 cm pathlength quartz cells, filled and sealed in the drybox, using a Cary 17 spectrophotometer versus a blank reference of the appropriate solvent. The densities of the 0.8:1 and 1.5:1  $\text{AlCl}_3$ :1-BPC melts were taken to be 1.231 and  $1.270 \text{ g ml}^{-1}$  at room temperature, respectively.

ACKNOWLEDGEMENT

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TABLE I

Ion mole fractions and equilibrium constants for titration of  $[\text{NiCl}_2] = 2.04 \times 10^{-3}$  in 1.5:1 melt, 40°C.

Emf V	$[\text{Ni}^{2+}]$ <sup>a</sup>	$[\text{Cl}^-]$ ion Excess to 1:1	$[\text{NiCl}_4^{2-}]$	$[\text{Cl}^-]$ <sup>b</sup>	K Values
-0.464	$2.15 \times 10^{-41}$	$8.57 \times 10^{-3}$	$1.72 \times 10^{-3}$	$1.69 \times 10^{-3}$	$1.02 \times 10^{-49}$
-0.504	$1.11 \times 10^{-42}$	$2.56 \times 10^{-2}$	$1.75 \times 10^{-3}$	$1.86 \times 10^{-2}$	$7.59 \times 10^{-47}$
-0.524	$2.51 \times 10^{-43}$	$4.38 \times 10^{-2}$	$1.78 \times 10^{-3}$	$3.67 \times 10^{-2}$	$2.56 \times 10^{-46}$
-0.551	$3.40 \times 10^{-44}$	$5.93 \times 10^{-2}$	$1.80 \times 10^{-3}$	$5.21 \times 10^{-2}$	$1.39 \times 10^{-46}$
-0.560	$1.74 \times 10^{-44}$	$7.47 \times 10^{-2}$	$1.83 \times 10^{-3}$	$6.74 \times 10^{-2}$	$1.96 \times 10^{-46}$
-0.586	$2.54 \times 10^{-45}$	$8.58 \times 10^{-2}$	$1.85 \times 10^{-3}$	$7.84 \times 10^{-2}$	$5.19 \times 10^{-47}$

a) Calculated from Nernst equation.

b)  $\text{Cl}^-$  ion fraction excess minus  $\text{Cl}^-$  combined with Ni(II).

Figure 1

Absorption spectra of  $\text{NiCl}_2$  dissolved in (a) 0.8:1  $\text{AlCl}_3$ :1-BPC melt,  
 $2.7 \times 10^{-3}$  M, (b) 1.5:1  $\text{AlCl}_3$ :1-BPC melt, nominal  $1.23 \times 10^{-4}$  M, at  
room temperature.

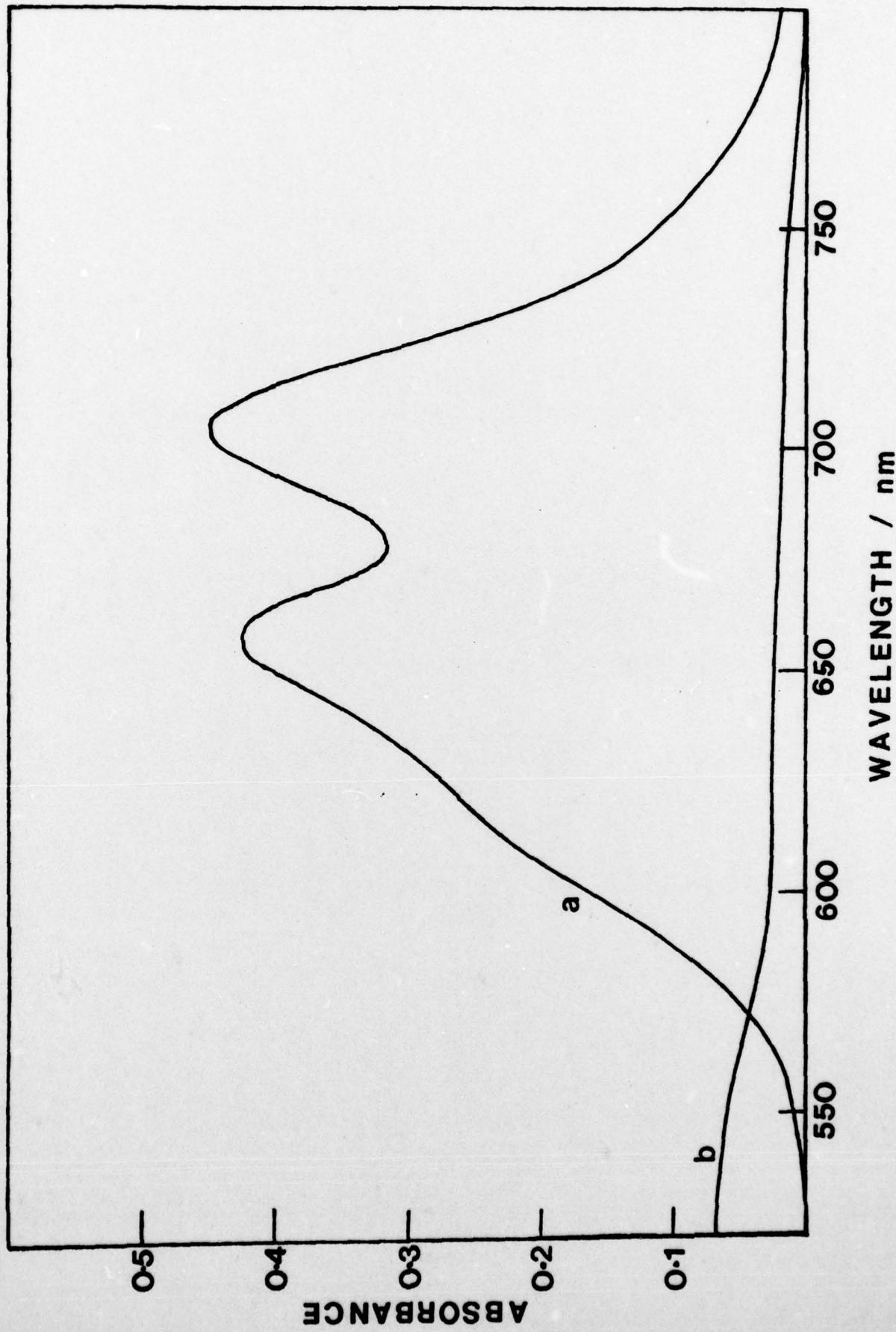


Figure 2

Cyclic voltammetry of Ni(II) in 1.5:1 melt at 40°, vitreous C electrode  
(area =  $0.0855 \text{ cm}^2$ ). Sweep rates, upper  $20 \text{ mVs}^{-1}$ , lower  $200 \text{ mVs}^{-1}$ . Nickel  
mole fraction =  $2.04 \times 10^{-3}$  added as  $\text{NiCl}_2$ .

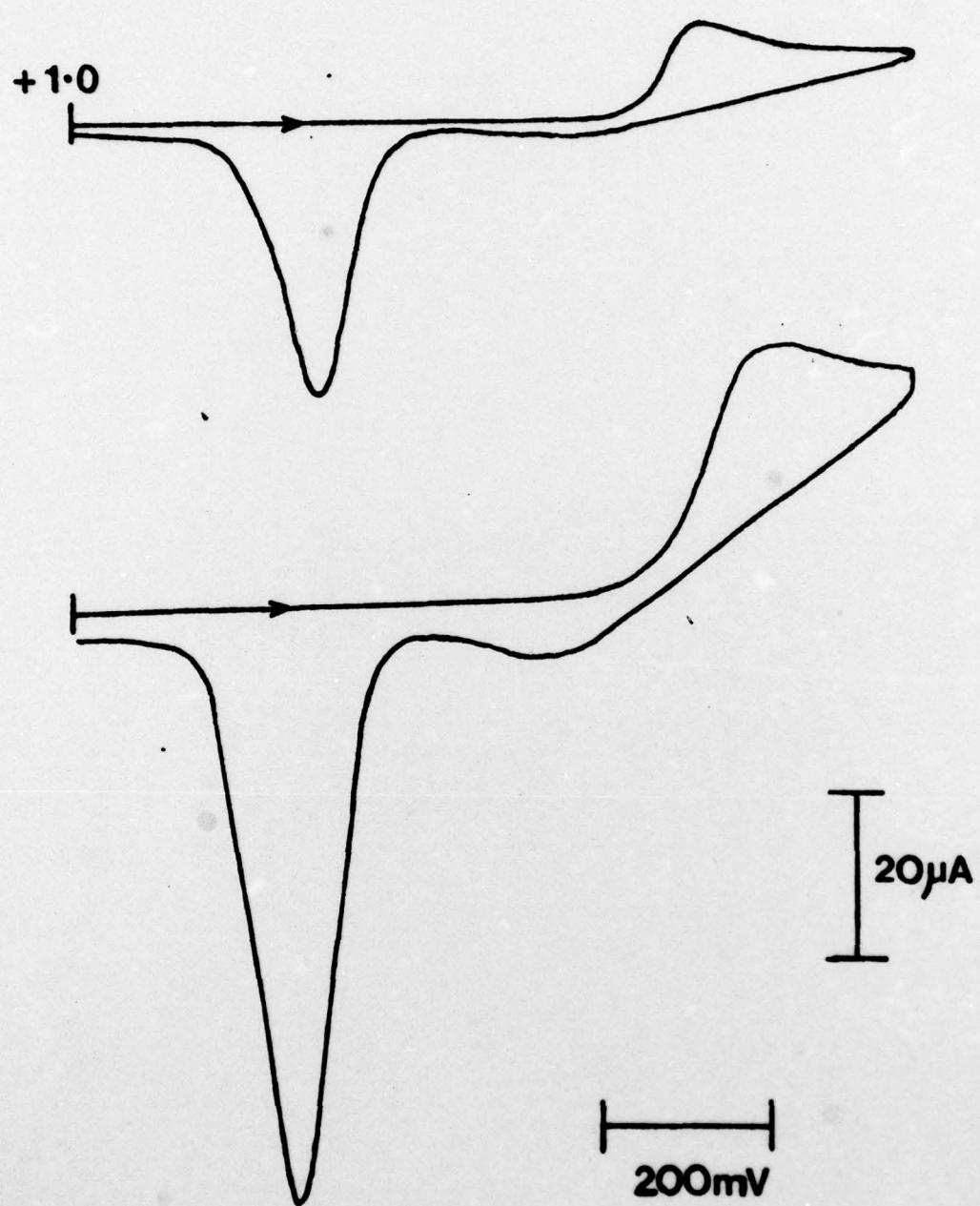
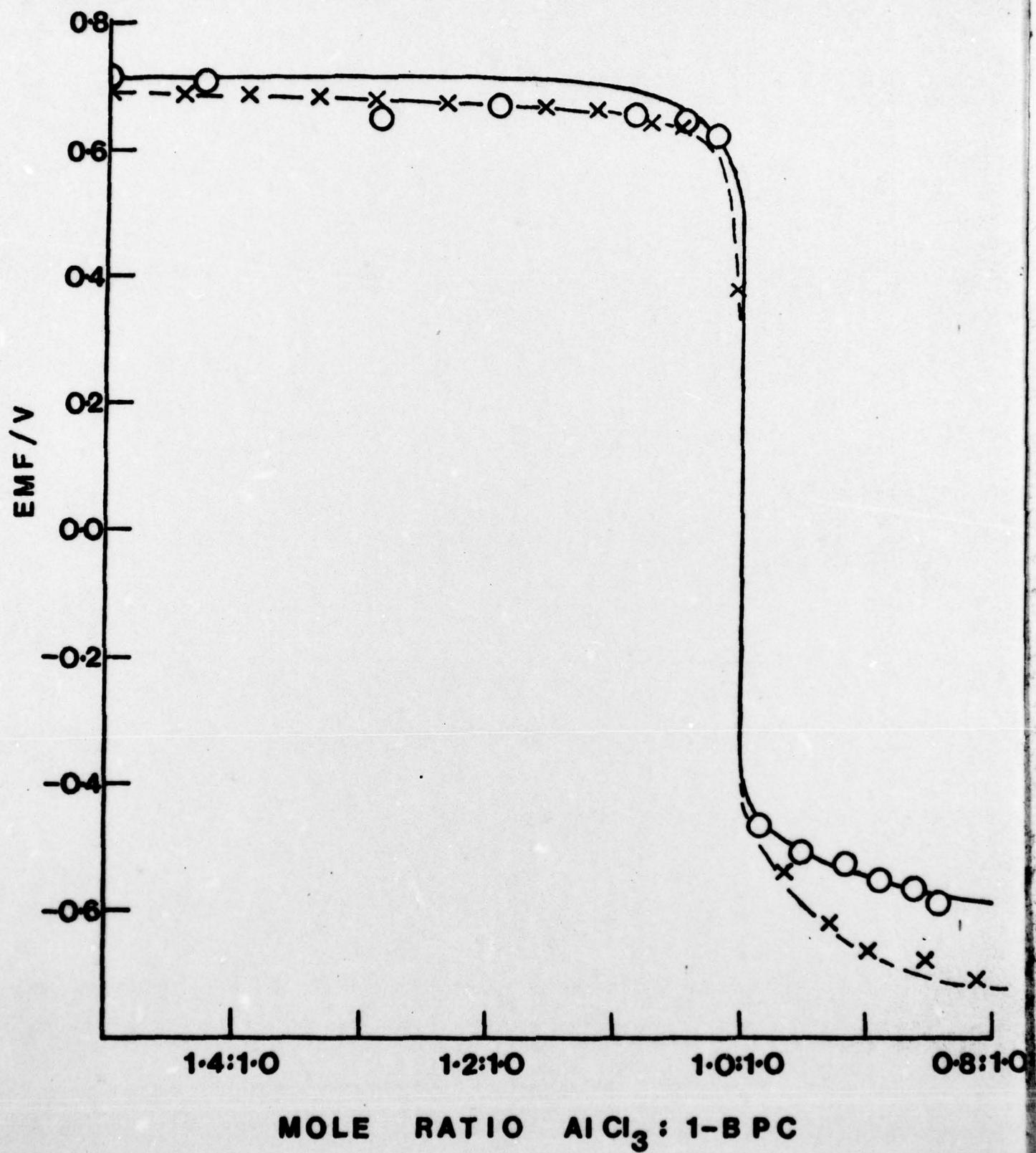


Figure 3

Potentiometric titration of Ni(II) by addition of 1-BPC; O 40°; x 150°.



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